

Optical Properties at X-ray Energies of Reflecting
Elements for Synchrotron Radiation Sources*

Summary

Preliminary results are reported for the optical constants at x-ray wavelengths of elements commonly used for x-ray mirrors and multilayer reflectors. The data were derived from measured absorption spectra using a dispersion theory-sum rule analysis.

Introduction

The optical properties of materials in the x-ray range are of increasing interest in conjunction with the development of instrumentation for synchrotron radiation sources,¹ particularly for the design of mirrors² and multilayer³ reflectors and filters. This letter is a preliminary report of a method for calculating these properties from presently available absorption data which are almost always fragmentary.

Theory

Generally, the only optical data⁴ available at x-ray wavelengths are for bulk absorption. In principle the other optical properties may be derived from these using the Kramers-Kronig relation⁵

$$n(\omega) - 1 = \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' k(\omega') d\omega'}{\omega'^2 - \omega^2}, \quad (1)$$

that connects the real and imaginary parts of the complex refractive index, $N(\omega) = n(\omega) + ik(\omega)$. The extinction coefficient $k(\omega)$ is related to the x-ray photoelectric mass absorption cross section $\mu(\omega)$, the quantity usually reported in the literature, by

$$k(\omega) = c\rho\mu(\omega)/2\omega, \quad (2)$$

where c is the speed of light in vacuum and ρ is the density of the material.

The primary difficulty in applying Eq. (1) is that knowledge of $k(\omega)$ for all ω is required. While good absorption data are generally available for hard x-ray energies, UV and soft x-ray data are often uncertain or fragmentary. This

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uncertainty at low energies would seem of minor importance for hard x-ray processes. However, we have found that systematic underestimates of oscillator strength in the low-energy portion of the data⁶ we analyzed gave errors in $n(\omega)-1$ exceeding 30-35% at $\hbar\omega > 5$ keV for roughly half the elements.

A means of circumventing this problem is evident from Eq. (1), which shows that the low-energy absorption contributes only a smoothly varying component to $n(\omega)$ at high energies. This contribution is proportional to the integrated oscillator strength at low energies, but is insensitive to its distribution. Thus, if the net absorption strength in the region of uncertainty can be estimated, a Kramers-Kronig analysis can be made despite the lack of reliable low-energy spectra.

A major guide to estimating the unknown or uncertain oscillator strength is the Thomas-Reiche-Kuhn f-sum rule^{7,8}

$$\int_0^\infty \omega k(\omega) d\omega = \pi^2 \mathcal{N} e^2 / m, \quad (3)$$

where \mathcal{N} , e , and m are the electron number density, charge, and mass, respectively. Provided reliable x-ray absorption data at high energies are available, their contribution to the f sum may be calculated and the remaining oscillator strength assigned to the low-energy region so that Eq. 3 is satisfied. In the cases in which the absorption of individual electron shells (or groups of shells) can be identified separately, an even more powerful guide is provided by partial f sums⁹. An example of this procedure is given by Shiles et al.¹⁰

Calculations

In the present study, the photoelectric cross sections above 10 eV as compiled by Biggs and Lighthill⁶ from experimental and theoretical sources were used. These consist of piece-wise continuous four-term polynomial fits to the absorption in regions bounded by the various absorption edges, a form particularly convenient for analytic integration of Eq. 1. To estimate the net absorption strength S below 10 eV we have used the f-sum rule, assuming the absorption to be concentrated at a single frequency ω_v ;

$$k(\omega) = S \delta(\omega - \omega_v), \quad 0 < \hbar\omega < 10 \text{ eV}, \quad (4)$$

where $\hbar\omega_v < 10$ eV. By Eq. (1)

$$\omega_v S = \pi^2 e^2 \mathcal{N} / m - \int_{10 \text{ eV}}^\infty \omega k(\omega) d\omega. \quad (5)$$

The properties at x-ray wavelengths are virtually independent of ω_v , but experience with materials for which UV refractive index data are available indicates that $\hbar\omega_v \sim 9.5$ eV is a reasonable choice.

The absorption below 10 eV is dominated by the most loosely bound electrons; hence, S is expected to be roughly equal to the number of valence electrons. In approximately half of the elements this expectation held for Biggs and Lighthill's cross sections.⁶ In these cases the refractive index was calculated directly from Eq. 1 using S determined via Eq. 5. A representative element in this group is aluminum, which has a total of 13 electrons per atom (e/a), three of which are loosely bound valence

electrons. In this case, the number n_{eff} of electrons effective in absorption from 10 eV to 1 MeV was found to be 10.18 e/a for the Biggs-Lighthill compilation.⁶ The specific distribution was found to be

Aluminum $Z = 13$

<u>Energy range (eV)</u>	<u>n_{eff} (e/a)</u>
10 to 73	.14
73 to 1,560	8.39
1,560 to 20,000	1.64
20,000 to 100,000	.01
100,000 to 0.5 MeV	3×10^{-4}
<u>0.5 MeV to 1 MeV</u>	<u>1×10^{-5}</u>
Total:	10.18

The remaining 2.82 e/a represents the valence-electron photoabsorption in the energy range 0 to 10 eV, a number that is in good agreement with the known valence.

In the second half of the elements -- particularly the transition elements -- S was significantly greater than the number of outer-shell electrons. From a study of partial f sums it became clear that this arose from a deficiency in absorption strength between 10 and 1,000 eV as reported by Biggs and Lighthill.⁶ In most cases this deficiency could be ascribed to an underestimate of absorption by weakly bound d or f electrons.

An example of an element in this second group is copper with 29 e/a. The Biggs-Lighthill data⁶ yielded the following distribution of oscillator strength:

Copper $Z = 29$

<u>Energy range (eV)</u>	<u>n_{eff} (e/a)</u>
10 to 100	4.64
100 to 933	6.17 ₅
933 to 1,096	1.58 ₅
1,096 to 8,981	6.26
8,981 to 100,000	1.42
<u>100,000 to 500,000</u>	<u>.013</u>
Total:	= 20.09

Since copper has 29 electrons per atom, the Biggs-Lighthill data⁶ implies that 8.91 electrons are effective in absorption below 10 eV. This is unreasonably high. Comparisons of n_{eff} were made with the optical absorption results given by Hagemann, Gudat, and Kunz¹¹ of DESY. These optical data indicate that only 0.9 e/a absorb in the 0 to 10 eV range, and hence, suggest an error in the Biggs-Lighthill⁶ work. In fact, for copper, Hagemann *et al.*¹¹ found that n_{eff} from 10 to 933 eV is 1.7 times larger than the values given in the above table, although n_{eff} was in agreement in other regions. For elements in this second group, the low-energy data of Biggs and Lighthill were scaled to make their integrated oscillator strength approximately equal to the occupation number of the shells involved in the absorption. This reduced S to approximately the number of valence electrons as expected. The optical constants were then calculated using the modified data.

IV. Results

The optical constants are best presented in terms of the complex atomic scattering factor for forward scattering:

$$f_1(0) = (m\omega^2/4\pi\rho e^2)[1 - \epsilon_1(\omega)], \text{ and } f_2(0) = (m\omega^2/4\pi\rho e^2)\epsilon_2(\omega), \quad (6)$$

where $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ denotes the complex dielectric function. Calculations for the 60² most common elements have been made to date. As an example, representative results for metallic platinum are given in Fig. 1.

Platinum Z=78

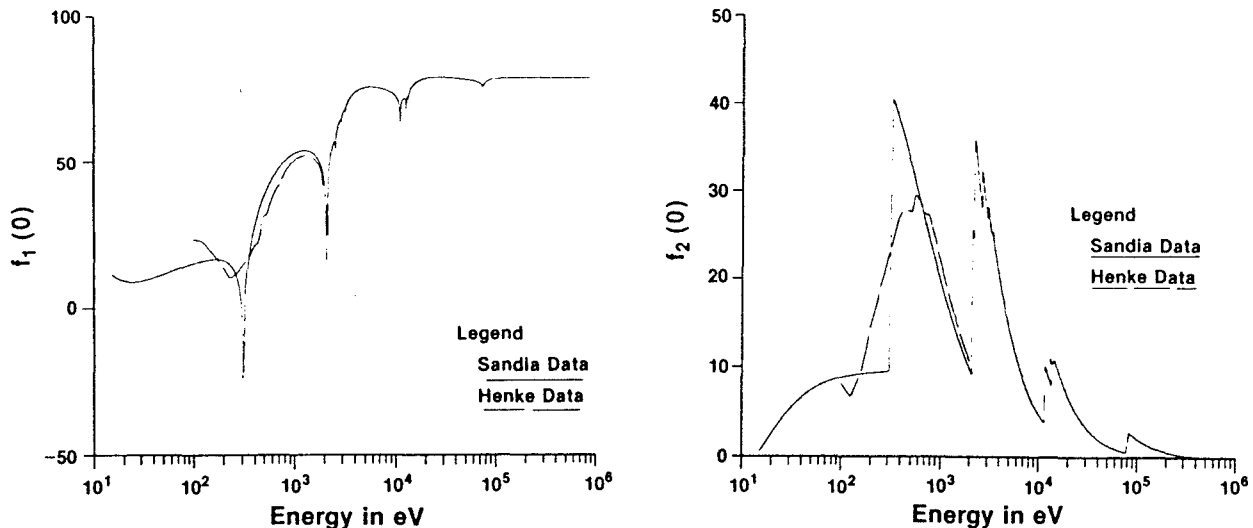
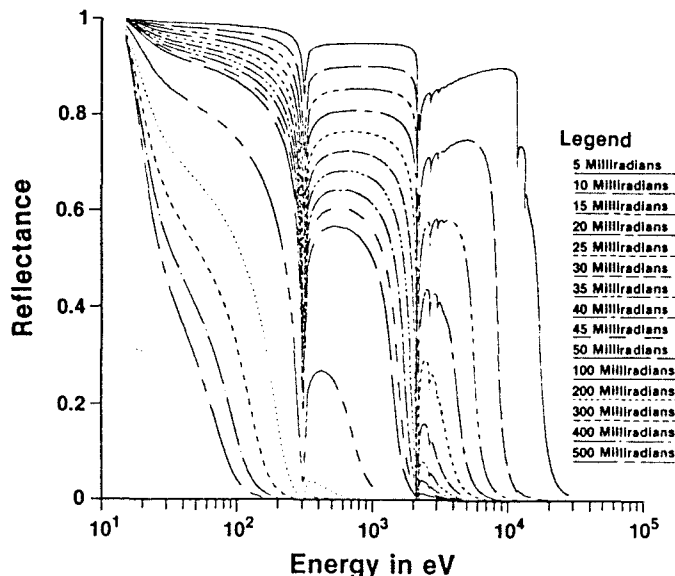


Fig. 1 The real and imaginary parts of the atomic scattering factor for forward scattering by metallic platinum. The solid curve was calculated from the cross-section data of Biggs and Lighthill, Ref. 6, in which the region below ~1 keV was treated approximately. The results of Henke *et al.*, Ref. 12, who studied the low-energy region in detail are shown for comparison.

The optical properties relevant to reflecting optical elements are the reflectance, critical angle for total external reflection, Brewster's angle, etc. Experience⁴ indicates that, at the energies of interest here, continuum electrodynamic theory holds approximately even though the x-ray wavelengths approach atomic dimensions. In particular, the reflectance as a function of angle may be calculated using the Fresnel equations.¹³ The results for the reflectance of a smooth platinum surface for unpolarized light are given in Fig. 2. (In practical mirrors these results must be reduced by a factor accounting for surface roughness, see Ref. 14.)

Fig. 2 The reflectance for unpolarized x-rays of a smooth surface of metallic platinum as calculated from the forward scattering factors given in Fig. 1 via the Fresnel equations. Angles are measured relative to the surface.

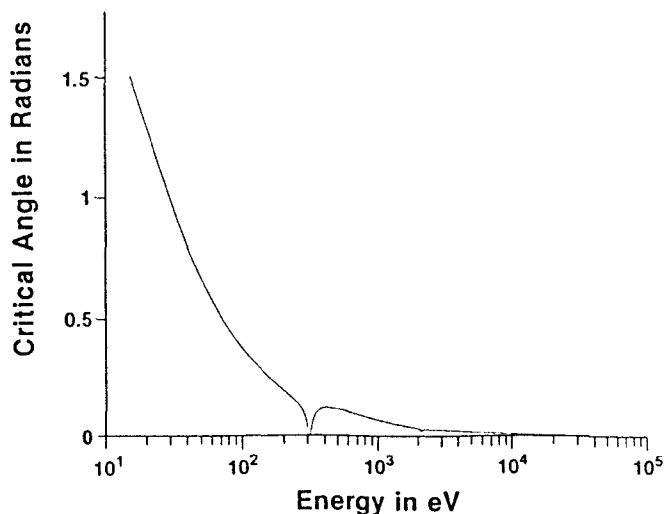


The critical angle for total external reflection θ_c (as measured relative to the surface) is given by

$$\theta_c(\omega) = \cos^{-1} n(\omega), \quad (7)$$

in the absence of absorption. Values of $\theta_c(\omega)$ for our exemplary substance platinum are given in Fig. 3. For $k \neq 0$ the reflectance, while not total, approaches unity for grazing angles less than θ_c provided the photon energy is not near an absorption edge,^{4,15} cf. Fig. 2.

Fig. 3 The critical angle (measured relative to the surface) for total external reflection for a smooth metallic platinum surface calculated via Eq. 7 from the forward scattering factors given in Fig. 1.



References and Footnotes

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